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(54) A method for the treatment of natural rubber field latex

(57) A method for the treatment of fresh natural rubber field latex comprises incubating the field latex with a proteolytic enzyme at a pH suitable for the enzyme. The amount of enzyme present and the incubation conditions are such that the enzyme-treated field latex, when subsequently processed into epoxidised natural rubber latex, has improved coagulation and crepeing properties.

A method for the preparation of epoxidised natural rubber from fresh natural rubber field latex is also described. This comprises i) incubating the field latex with a proteolytic enzyme at a pH suitable for the enzyme, ii) epoxidising the enzyme-treated field latex to the desired mole % level of epoxidation, iii) coagulating the epoxidised natural rubber latex, and iv) crepeing, washing, crumbling and drying the epoxidised natural rubber.

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SPECIFICATION

A method for the treatment of natural rubber field latex

This invention relates to the use of natural rubber (NR) field latex for the production of epoxidised natural rubber (ENR). In particular it relates to a method of treatment of NR field latex so that ENR can be prepared from it.

Epoxidised natural rubber is a relatively new form of rubber which has some useful properties similar to those possessed by more specialised rubbers. For example, depending on the level of epoxidation, it has low gas permeability, good oil resistance, good wet grip, low rolling resistance and high damping. The epoxidation of natural rubber and other unsaturated polymers is well known. ENR may be prepared from centrifuged latex concentrates which is a few weeks old (hereinafter referred to as "matured latex concentrate") by epoxidation with peracetic or performic acid under controlled conditions. After the epoxidation reaction, the latex is coagulated and the coagulated rubber is converted to crumbs which are then dried with through circulation of hot air. Since the epoxidation is carried out under acidic conditions, the latex is stabilised with a non-ionic surfactant during the reaction. It is well known that latex stabilised with a non-ionic surfactant can be coagulated by heating to a temperature close to the cloud point of the surfactant. Large scale production of ENR involves the following steps:

(a) epoxidation of the latex,
(b) coagulation of the latex with steam,
(c) crepeing and washing of the coagulum and hammermilling the crepe to form crumbs,
(d) chemical treatment to improve properties,
(e) drying of the crumbs and
(f) pressing and palleting of the dried crumbs.

For the production of 50 mole % epoxidised natural rubber (ENR50) latex from matured latex concentrate it is usual to add 25 parts per hundred parts rubber (phr) of common salt to the latex to lower its colloidal stability before coagulating the latex by passing steam directly into the latex held in containers. This is a batch-wise process. The coagulum is allowed to consolidate or mature for 2 hours and then passed through the crepeing mill or a series of crepeing mills. After one pass through the creper, a continuous sheet or crepe is formed. The crepe is usually passed through the creper many times (about 8 times) before it is comminuted to crumbs in a creper-hammermill. These operations, i.e. step (c) of the above process, are important because besides dewatering the coagulum they also facilitate the removal from the coagulum of excess water soluble reactants and reaction by-products which, if they were to remain, could cause adverse properties in the rubber.

The processing of the ENR50 coagulum into dry crumbs uses the same conventional machinery and equipment as that used for producing crumb rubber e.g. Heveacrumb.

However, if the starting material for epoxidation is fresh NR field latex, rather than matured latex concentrate, the ENR latex (ENR50 and ENR25) obtained is very much more difficult to coagulate by heating with direct steam even with the addition of common salt. It requires a longer period of heating for coagulation to occur and this gives rise to a lot of very fine particles; however, coagulation is even then still incomplete. After maturation of the coagulum for a few hours or even overnight, the coagulum, on repeated passage through the creper, does not form a crepe but breaks up into small pieces and into fine particles. In fact the coagulum behaves somewhat like a paste. The fine particles can be dispersed in water to give a milky dispersion resembling a latex. Hence it is difficult to dewater the coagulum and to wash excess reactants and reaction by-products off the rubber without the loss of a great deal of the rubber itself. Moreover, this paste-like coagulated rubber is difficult to dry. As a result, ENR latex prepared from fresh field latex cannot be economically processed into dry rubber using the conventional rubber processing machinery and equipment.

A newer method for coagulating ENR latex, which is infact preferred, is the continuous coagulation method using the apparatus and method described in our UK Patent Application No. 8427736. According to this method, ENR latex is passed down a substantially vertical stainless steel column as a thin film on the inner surfaces thereof until it comes into contact with steam which has been introduced into the interior of the column, whereupon the latex is rapidly heated by the steam and coagulates. The resulting coagulum passes through the remainder of the column and is collected at the exit thereof.

ENR50 latex prepared from matured latex concentrate can be coagulated in the column coagulator but the matured coagulum breaks up into small pieces and into fine particles on the creper. If the small pieces of coagulum are repeatedly passed through the creper, a crepe is formed after 5 to 10 passes through the creper; the finer particles, however, still do not form a crepe. ENR25 latex prepared from matured latex concentrate may also be coagulated by this method and the coagulum can be converted to crepe and crumbs without much difficulty.

However, in the case of ENR50 or ENR25 latex prepared from fresh field latex, the latex does not coagulate in the column coagulator. Sometimes the latex merely thickens slightly and some flocs are formed which even on maturation behave somewhat like a paste and do not form a crepe even on repeated passage through the creper.

In many rubber-producing countries, it would be more economical to use fresh field latex instead of matured latex concentrate as the starting material from which ENR is prepared. However, in view of the aforementioned problems this has so far not been possible. These problems are rather unique and it is believed that difficulties

of a similar nature have not been encountered before in the processing of natural rubber latex into dry rubber. It is to be understood that the term "field latex" as used herein includes field latex in which the bottom fraction and sludge have been removed by clarifying with a centrifugal clarifier.

There are a number of differences between fresh field latex and matured latex concentrate, such as a difference in particle size. However, it may be supposed that for present purposes the most important difference is the presence of a much larger amount of non-rubber substances in field latex. There are a lot of non-rubber substances in natural rubber latex including the following classes of substances: inositols, carbohydrates, proteins, lipids, amino acids, other organic acids, nitrogeneous bases, thiols, nucleic acids and metallic cations and inorganic anions. It may seem obvious to try to solve the problems by removing the non-rubber substances, but it is not at all obvious as to which of these are causing the problems.

British Patent No. 1,366,934 describes a method of removing protein from natural rubber which comprises incubating natural rubber latex with a proteolytic enzyme at a pH suitable for the enzyme in the presence of a soap to prevent premature thickening or coagulation of the latex and subsequently separating proteinaceous material from the rubber. The resulting deproteinised natural rubber (DPNR) contains not more than 1% of proteinaceous material.

It has now been found that the afore-mentioned problems associated with the use of fresh field latex for the production of epoxidised natural rubber are caused by the presence of a large amount of protein in the field latex and, more specifically, it is the molecular size of the proteins which causes the problems.

According to the present invention there is provided a method for the treatment of fresh natural rubber field latex which comprises incubating the field latex with a proteolytic enzyme at a pH suitable for the enzyme, the amount of enzyme present and the incubation conditions being such that the enzyme-treated field latex, when subsequently processed into epoxidised natural rubber latex, has improved coagulation and crepeing properties.

According to a further embodiment of the present invention there is provided a method for the preparation of epoxidised natural rubber from fresh natural rubber field latex which comprises the following steps:-
i) incubating the field latex with a proteolytic enzyme at a pH suitable for the enzyme,
ii) epoxidising the enzyme-treated field latex to the desired mole % level of epoxidation,
iii) coagulating the epoxidised natural rubber latex, and
iv) crepeing, washing, crumbling and drying the epoxidised natural rubber.

The latex to be treated with enzyme could also be skim latex or field latex to which some skim latex has been added before epoxidation.

It has been found that a limited enzyme treatment of fresh or matured latex concentrate before epoxidation to high epoxidation levels (e.g. ENR 50) enables the epoxidised latex to be coagulated using either the batch coagulation method or the continuous column coagulation method without the need to add common salt to the latex and the resulting coagulum has good crepeing properties.

The present invention therefore provides a way of overcoming the previously described problems by providing a method of reducing the size of the protein molecules in the field latex by enzymatic hydrolysis using any proteolytic enzyme. The level of enzyme added to the field latex and the incubation time are very important and are much greater than those required for preparing enzyme deproteinised natural rubber by the previously known method referred to above. After the enzyme treatment, it is not necessary to remove the degraded protein fragments from the latex. The enzyme-treated field latex, after the appropriate incubation period, is ready for epoxidation to the required mole % epoxidation level. The ENR latex thus prepared can be successfully coagulated by steam according to either (a) the batch coagulation method, or (b) the continuous coagulation method. In both processes of coagulation, no addition of common salt to the latex is required.

In the batch coagulation method, steam is passed directly into the ENR latex held in a series of containers until the temperature reaches about 98°C. The hot coagulum is left to mature typically for from about 1/2 hour to 3 hours. During this period the smaller pieces of coagulum consolidate and form a big and quite coherent mass. Coagulation is completed giving a clear serum. During the maturation period, the coagulum is tested at intervals for its ability to form a crepe after one pass through the creper. As soon as this is possible the coagulum is creped and washed about 8 times and is then comminuted to crumbs using the creper-hammermill. For the final size-reduction other conventional machinery, e.g. a creper-shredder or extruder or pelletiser, may also be used. The crumbs are then dried with through circulation of hot air (about 80°C to 100°C) in the usual way. It is not advisable to leave the hot coagulum to mature for longer than is necessary as excessive heat is known to degrade the rubber molecules. Maturation of the hot coagulum for different periods of time may be used to prepare ENR of varying molecular weight and hence generally different Mooney viscosity.

In the continuous coagulation method, the ENR latex is passed down a vertical stainless steel column and is coagulated with steam inside the column as described earlier. The coagulum is collected in a container placed at the exit of the column. It is then left to mature typically for from 1/2 hour to 3 hours and is then creped and washed and converted to crumbs and dried in a similar way as in the batch coagulation method. For this method to work effectively, it is desirable for the ENR latex to have a dry rubber content of about 25% or higher.

In the present process, we have used Savinase 8.0L and Alcalase 2.5L both of which are alkaline proteinases but other proteolytic enzymes may be used. Both these enzyme preparations are commercially available. These are supplied in liquid form and consist of the active enzyme dissolved in a solvent system consisting of 1,2-propanediol, stabiliser and water. Savinase 8.0L has an activity of 8.0 Kilo Novo Proteinase Units per gram

(KNPU/g) while Alcalase 2.5L has an activity of 2.5 Anson Units per gram (AU/g).

The physical form of the enzyme is not important, for example Alcalase 2.0T which is available as dry granules having an activity of 2.0 AU/g has also been used successfully. A disadvantage of using the granular form is that the inert carrier, e.g. titanium dioxide, which is insoluble in water must be removed by sedimentation or centrifugation after the enzyme has been dissolved. This operation results in the loss of some of the enzyme. Moreover, if sedimentation is used to remove the inert carrier, a dilute solution of about 5% must be prepared to obtain maximum recovery of the enzyme solution. This dilute enzyme solution causes undesirable dilution of the field latex.

The amount of enzyme may be chosen to obtain a desired rate or degree of proteolysis. We have used 0.05 to 1 phr of the liquid enzyme for fresh field latex. Time and temperature of incubation may also be chosen to achieve the desired rate and degree of proteolysis, typical figures being from 12 to 96 hours at from 25°C to 60°C. The pH range for the enzymes is from 7.5 to 11.0. It will be appreciated that if the enzymatic hydrolysis is carried out at a high temperature (40-60°), the incubation time and/or the level of enzyme required can be reduced.

The amount of enzyme and the time of incubation are very important. Low levels of enzyme and short incubation times which are sufficient for preparing DPNR are inadequate for solving the problems of coagulation and crepeing satisfactorily. These are illustrated in Examples 1 to 3. For the preparation of DPNR as described in British Patent No. 1,366,934 the latex after incubation with enzyme is diluted to a solids content of about 3% prior to coagulation with acid so as to avoid entrapping proteinaceous material in the coagulum. We have used this method to assess approximately the extent of protein breakdown using different levels of enzyme and different incubation times. This is illustrated in Example 1. The nitrogen content of the DPNR provides some indication of the extent of protein breakdown.

The ENR produced from enzyme-treated field latex has a low nitrogen content, typically about 0.04% on the weight of the rubber. This value is even lower than the lowest value obtained, about 0.06%, for DPNR prepared by enzyme deproteinisation of field latex (Example 1). The reason for this is probably due to further hydrolysis of the enzyme-degraded protein fragments and/or hydrolysis of other nitrogen-containing compounds (e.g. phospholipids) under the conditions of the epoxidation reaction, i.e. heat and performic acid. The increased solubility of the protein fragments during the heat coagulation of the ENR latex could also account for this lower value. The ash content of the ENR is typically 0.08% by weight. It is noted that the nitrogen content of ENR prepared from matured latex concentrate is about 0.11% on the weight of the rubber.

If it is desired to improve the properties of the ENR e.g. Wallace plasticity and plasticity retention index, this may be achieved using known chemical methods. For example an antioxidant may be added to the latex before coagulation and the ENR crumbs may be treated with an antioxidant before drying.

It is not fully understood why enzymatic hydrolysis of the proteins in field latex should solve the problems of difficulty in coagulation of ENR latex and inability of the coagulum to form a crepe, but it seems likely that the following factors contribute to the result. Under the epoxidation conditions which consist of heating the latex with formic acid and hydrogen peroxide in the presence of a non-ionic surfactant, (a) the protein molecules are chemically converted to some form of steric stabiliser and/or (b) the protein molecules interact chemically with the non-ionic surfactant to form bigger steric stabiliser molecules. (Non-ionic surfactants are steric stabilisers themselves). These protein-derived steric stabiliser molecules have the effect of inhibiting or reducing the probability of the latex particles cohering and coalescing with one another to form a quite continuous and coherent mass, when collision between particles occurs at temperatures of less than about 100°C. Hence the ENR latex is difficult to coagulate by heating with steam. In the presence of salt the protein-derived steric stabiliser and the non-ionic surfactant gradually lose some of their stabilisation property towards heat. Hence on heating the ENR latex in the presence of common salt, some coagulation occurs; this is the result of rubber particles coalescing to form loose aggregates. Depending on the size, each loose aggregate contains many rubber particles having some contact with one another but because of the presence of the protein derived steric stabiliser molecules on the surface of the particles, the latter are inhibited or hindered from further coalescing with one another to form a bigger and quite continuous and coherent mass. The loose aggregates are also similarly inhibited or hindered from coalescing with one another to form a bigger mass. In fact the matured coagulum on passing through the creper breaks up into loose aggregates.

When the protein molecules are hydrolysed into small fragments e.g. polypeptides and amino acids and under the epoxidation reaction conditions, the reaction products that may be formed from these small fragments have a lower steric stabilisation property compared with the very much bigger protein-derived steric stabiliser; the smaller the fragments, the lower is the stabilisation property. This probably explains why a higher level of enzyme and longer incubation time which result in a greater degree of proteolysis are more effective in solving the problems described.

The following examples are included to illustrate the present invention.

Example 1

Field latex was preserved with 0.25% ammonia on latex weight. Potassium oleate was added to the latex at a level of 1 phr to stabilise the latex when the proteins were degraded. The enzymes, Savinase 8.0L and Alcalase 2.5L, were aded to two samples of the latex at levels of 0.1 to 0.5 phr and the latex mixtures were incubated at room temperature (about 30°C) for 1 to 6 days.

After various incubation periods, a sample of each latex was diluted to a solids content of about 3% before

coagulation with formic acid in the usual way. The coagulated rubber was creped and dried in warm air in the usual way. The nitrogen content of the rubber is given in Table 1.

TABLE 1 Nitrogen content of rubber (weight %) from field latex treated with Savinase and Alcalase

Enzyme level, phr / *Days*	*0.10*	*0.15*	*0.20*	*0.30*	*0.40*	*0.50*
1	0.08 (0.25)	0.09 (0.13)	0.08 (0.09)	0.08 (0.10)	0.06 (0.08)	0.08 (0.10)
2	0.09 (0.09)	0.08 (0.08)	0.07 (0.09)	0.08 (0.09)	0.06 (0.07)	0.07 (0.07)
3	0.07 (0.08)	0.06 (0.07)	0.06 (0.07)	0.06 (0.06)	0.06 (0.06)	0.07 (0.07)
4	0.07 (0.07)	0.07 (0.07)	0.07 (0.07)	0.07 (0.06)	0.06 (0.07)	0.07 (0.06)
6	0.07 (0.06)	0.07 (0.07)	0.06 (0.07)	0.07 (0.08)	0.07 (0.08)	0.06 (0.07)

Unbracketed values are for Savinase treated latex while bracketed values are for Alcalase treated latex. Nitrogen content of control rubber (i.e. no enzyme treatment) = 0.35%

It is seen that for an incubation time of 1 day and at enzyme levels of less than about 0.2 phr, Savinase 8.0L is more effective than Alcalase 2.5L but at longer incubation times both enzymes are equally effective in hydrolysing the proteins in the latex.

Example 2

Fresh field latex was preserved with 0.25% by weight of ammonia (System A) or 0.25% by weight of ammonia plus 0.013% of tetramethyl thiuram disulphide (TMTD) and 0.013% of zinc oxide (System B). Preservative system B is known to keep field latex stable and fluid for a longer period than system A. Non-ionic surfactant (e.g. Teric 16A29) used to stabilise the latex for the epoxidation reaction was added at a level of 2 phr. (Teric 16A29 is a condensation product of one molecule of a long chain aliphatic alcohol mainly cetyl alcohol and about twenty nine molecules of ethylene oxide.) The liquid enzyme preparation was added to the latex mixture which was then allowed to incubate at room temperature for 24 to 66 hours. After incubation the latex was epoxidised to ENR50 by heating with formic acid and hydrogen peroxide for about 24 hours. The reaction was then stopped by neutralising the acid with ammonia. The ENR50 latex was then coagulated with steam by either (a) the batch coagulation method or (b) the continuous coagulation method.

In the batch coagulation method, steam was passed directly into the latex in a series of containers until the temperature reached about 95°C. The latex coagulated and the coagulum was left to mature typically for about 1/2 hour to 3 hours until it could form a creped after one pass through the creper. It was then crepe and washed about 8 times and then size-reduced to crumbs on the creper-hammermill in the usual way. The crumbs were dried with through circulation of hot air in the usual way.

In the continuous coagulation method, the ENR50 latex was passed down a vertical stainless steel column as a thin film and was coagulated with steam inside the column as described in UK Patent Application No. 8427736. The coagulum was collected in container placed at the exit of the column. It was then left to mature typically for 1/2 hour to 3 hours and was creped and washed 8 times and converted to crumbs and dried in a similar way as for the batch coagulation method. For this method to work effectively it is desirable for the ENR50 latex to have a dry rubber content of about 25% or more.

The conditions for enzyme treatment and their effect upon the coagulation of ENR50 latex and the ability of the coagulum to form a crepe are shown in Table 2.

TABLE 2 Effect of enzyme treatment conditions on the coagulation and crepeing of ENR50

	Experimental field latex	*Enzyme level,phr*	*Incubation Time,hours*	*Coagulation*	*Crepeing*
1.	System A	Nil	—	poor	cannot form crepe
2.	System A	0.40 Savinase	24	good	poor
3.	System A	0.25 Savinase	42	good	poor
4.	System A	0.25 Savinase	66	good	good
5.	System A	0.25 Alcalase	66	good	good
6.	System B	0.35 Savinase	42	good	good
7.	System B	0.35 Alcalase	42	good	good

Good coagulation indicates that complete coagulation occurred, while poor coagulation indicates that coagulation was either incomplete or little coagulation occurred.
Good crepeing indicates that the coagulum formed a crepe after 1 pass through the creper, while poor crepeing indicates that many passes were needed before a crepe was formed.

The nitrogen contents of the NER50 obtained were 0.03 to 0.04 weight % for Experiments (2) to (7). These values were lower than those of ENR50 (average = 0.11 weight %) prepared from matured latex concentrate or those of DPNR from enzyme deproteinisation of field latex shown in Table 1. The average ash content of the ENR 50 (45 samples) prepared according to Experiments (4) to (7) was 0.08% by weight with a standard deviation of 0.02%.

It is seen that the presence of a small amount of TMTD and zinc oxide in the latex did not affect the effectiveness of the enzymes used.

From Table 2, it is noted that the level of enzyme added and the time of incubation are very important in order to solve the problems of coagulation and crepeing satisfactorily. Low levels of enzyme and short incubation times which are sufficient for preparing DPNR (Table 1) are inadequate for solving these problems satisfactorily.

Example 3

Fresh field latex was preserved with 0.25% by weight of ammonia and stabilised with 1.6 phr of non-ionic surfactant (e.g. Teric 16A29) and then treated with Savinase 8.0L. After incubation the latex was epoxidised to ENR25 by heating with formic acid and hydrogen peroxide for about 24 hours. The reaction was then stopped by neutralising the acidic latex mixture with ammonia. The latex was coagulated with steam by either (a) the batch coagulation method or (b) the continuous coagulation method and the coagulum was creped and converted to crumbs and dried in a similar way as for ENR50 in Example 2. The initial sizes of the rubber flocs appeared to be smaller than those of ENR50. However, on maturation for 1/2 hour to 2 hours, these flocs consolidated into a big mass which could be creped and converted to crumbs without problems if enzymatic hydrolysis was sufficient.

The effect of the conditions of enzyme treatment on the coagulation of ENR25 latex and crepeing behaviour of the coagulum is shown in Table 3.

TABLE 3 Effect of enzyme treatment conditions on the coagulation and crepeing of ENR25

Experiment	*Savinase level,phr*	*Incubation Time,hours*	*Coagulation*	*Crepeing*
1	0.3	42	poor	—
2	0.4	66	poor	—
3	0.6	66	good	good
4	0.40	96	good	good

The nitrogen content of the ENR25 obtained was 0.04 weight % for Experiments (3) and (4) and the ash content was similar to those of ENR50 in Example 3.

Example 4

This example demonstrates heat accelerated enzymatic hydrolysis.

The incubation time and/or the level of enzyme needed can be reduced by accelerating the enzymatic hydrolysis of the proteins present in field latex. This is achieved by carrying out the hydrolysis at elevated temperature (e.g. 40°C – 60°C). It has been found that it is not necessary to maintain the temperature of the enzyme-treated latex at a constant level. Hence on day zero 4000 litres of enzyme-treated field latex (treated in a similar way as in Example 2 for ENR 50 and Example 3 for ENR 25) were heated to 55°C, whereupon the heating was discontinued to save energy (and thus reduce costs). The latex mixture was covered and left undisturbed overnight (about 18 hours) so that the hydrolysis could proceed. The next day (day one) the

temperature of the latex was found to have dropped to about 46°C. At the end of this 18 hour enzyme treatment, the latex was ready for epoxidation to ENR 50 in a similar way as in Example 2.

For a 42 hour enzyme treatment, the latex was again heated to 55°C on day one, whereupon the heating was discontinued and the latex left undisturbed for 24 hours. It was then epoxidised to ENR 50 in a similar way as in Example 2 or epoxidised to ENR 25 as in Example 3.

Similarly for a 66 hour enzyme treatment, the latex was again heated to 55°C on day two, the heating was then discontinued and the latex left for another 24 hours. It was then epoxidised to ENR 25 in a similar way as in Example 3.

The epoxidised latex, after neutralisation with ammonia, was coagulated with steam by either (a) the batch coagulation method or (b) the continuous column coagulation method and the coagulum was creped and converted to crumbs and dried in a similar way as in Example 2.

The effects of the above conditions of heat and enzyme treatment on the coagulation of epoxidised latex and the crepeing behaviour of the coagulum are shown in Table 4.

TABLE 4: Effect of enzyme treatment conditions (45° – 55°C) on the coagulation and crepeing of ENR 50 and ENR 25

Experiment	*Enzyme level, phr*	*Incubation Time, hours*	*Coagulation*	*Crepeing*
1. ENR 50	0.25 Alcalase	18	Good	Poor
2. ENR 50	0.40 Alcalase	18	Good	Good
3. ENR 50	0.40 Savinase	18	Good	Good
4. ENR 50	0.20 Alcalase	42	Good	Poor
5. ENR 50	0.30 Alcalase	42	Good	Good
6. ENR 50	0.30 Savinase	42	Good	Good
7. ENR 25	0.55 Alcalase	42	Good	Good
8. ENR 25	0.35 Alcalase	66	Good	Good
9. ENR 25	0.35 Savinase	66	Good	Good

Alcalase refers to Alcalase 2.5 L while Savinase refers to Savinase 8.0. L.

For ENR 25, the coagulation of the epoxidised latex (Experiments 7 to 9) was much better than that in Experiments 3 & 4 of Example 3 since the initial sizes of the coagulated rubber appeared to be bigger and therefore the coagulum could be creped in a shorter time.

The nitrogen and ash contents of the epoxidised rubbers were similar to those in Examples 2 & 3.

CLAIMS

1. A method for the treatment of fresh natural rubber field latex which comprises incubating the field latex with a proteolytic enzyme at a pH suitable for the enzyme, the amount of enzyme present and the incubation conditions being such that the enzyme-treated field latex, when subsequently processed into epoxidised natural rubber latex, has improved coagulation and crepeing properties.

2. A method as claimed in claim 1, wherein the natural rubber field latex is incubated with from 0.05 to 1 phr of a proteolytic enzyme having an activity of 8.0 KNPU/g enzyme of 2.5 AU/g enzyme for from 12 to 96 hours at from 25°C to 60°C.

3. A method as claimed in claim 1 or claim 2, wherein Savinase or Alcalase or other alkaline proteinase is used as the enzyme at a pH of from 7.5 to 11.

4. A method as claimed in any one of claims 1 to 3, wherein a non-ionic surfactant is present at a level of from 1 to 5 phr so to stabilise the latex during the enzyme treatment and prevent premature coagulation.

5. Epoxidised natural rubber latex which has been prepared from natural rubber field latex treated according to the method as claimed in any one of claims 1 to 4.

6. A method for the preparation of epoxidised natural rubber from fresh natural rubber field latex which comprises the following steps:-

i) incubating the field latex with a proteolytic enzyme at a pH suitable for the enzyme,

ii) epoxidising the enzyme-treated field latex to the desired mole % level of epoxidation,

iii) coagulating the epoxidised natural rubber latex, and

iv) crepeing, washing, crumbling and drying the epoxidised natural rubber.

7. A method as claimed in claim 6, wherein the epoxidation of step ii) is performed by heating the enzyme-treated field latex with formic acid and hydrogen peroxide.

8. A method as claimed in claim 6 or claim 7, wherein the coagulation of step iii) is performed by passing steam directly into the epoxidised natural rubber latex until the temperature reaches about 98°C.

9. A method as claimed in claim 6 or claim 7, wherein the coagulation of step iii) is performed by passing the epoxidised natural rubber latex down a stainless steel column counter-current to steam.

10. A method as claimed in any one of claims 6 to 9, wherein additional chemicals, such as an antioxidant, are added to the epoxidised natural rubber latex before coagulation and/or to the epoxidised natural rubber crumbs before drying.

11. Epoxidised natural rubber which has been prepared from natural rubber field latex treated according to the method as claimed in any one of claims 1 to 10 and wherein the nitrogen content is not more than 0.08% by weight.

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